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# Viewpoint: How to gain atomistic insights on reactions at the water/solid interface?

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## **Abstract**

Reactions at the water/solid interface are central to the development of sustainable processes, from biomass upgrading to photo- and electrocatalysis. To gain atomistic insight in these reactions, modelling approaches have been constantly improved over the past decade. Polarizable continuum models have considerably improved the description of charge separation and enabled a proper inclusion of the surface polarisation in electrochemistry and photocatalysis. Micro-solvation has been used to probe the impact of H-bonding at the water/catalyst interface, a key ingredient to explain observed solvent effects in liquid heterogeneous catalysis. Last, considerable efforts have been dedicated to reach a full atomistic description of the water/liquid interface, allowing the evaluation of activation energies of catalytic reactions and catalyst decomposition. In this Viewpoint, we illustrate advantages and limitations of current methods and provide perspectives.

## Keywords

Solvation, solid/water interface, catalysis

## View Point

Aqueous interfaces are ubiquitous and central to a wide range of important and challenging processes: rock weathering in geochemistry, bio-compatibility of materials, and in aqueous phase heterogeneous catalysis including biomass upgrading, electro- and photocatalysis.<sup>1-3</sup> The fundamental knowledge of these interfaces is surprisingly limited compared to solid/gas interfaces and bulk water. For example, open questions remain regarding the water structuring, the possible water dissociation at the interface, the impact of an applied electrochemical potential on this interfacial structure and the consequences of interfacial solvation effects on catalytic reactions.<sup>3</sup> Standard surface sciences techniques (STM, vibrational and X-Ray spectroscopy, etc.) cannot be easily applied to the solid-liquid interface.<sup>1</sup> Nevertheless, they can provide valuable information about the interaction of water with surfaces under surface-science conditions (low pressure).<sup>4</sup> For instance, in conjunction with DFT calculations,<sup>5,6</sup> several groups have found that water dissociates above 150 K and forms a mixed (OH/H/H<sub>2</sub>O) overlayer on Ru(0001).<sup>4</sup> Still, surface sciences techniques are limited to one or few layers of water at low temperature, which is a questionable approximation for liquid water at room temperature or typical reaction conditions for biomass transformations, which can reach  $\sim 200$  °C in an autoclave.<sup>7</sup> Other methods can be used (e.g. calorimetry and inelastic neutron scattering<sup>2</sup>) and some are even specifically designed to be sensitive to the interfacial signal, such as non-linear optical spectroscopies<sup>8,9</sup> and surface sensitive X-Ray diffraction methods.<sup>9,10</sup> In all these studies, modelling appears as a corner-stone to convert the experimentally measured signals into an atomistic understanding of aqueous interfaces involved in catalysis. Several modelling approaches have been developed and used in the past decade. We here discuss

how to choose the best method depending on the expected role of water on the reaction investigated at the catalyst/water interface, building on the experience we accumulated during the past years on a wide range of systems.

To model reactions at the catalyst/water interface, *implicit solvent models*, also known as polarisable continuum models (PCM), have been used increasingly since it was first implemented in a major periodic DFT software in 2014,<sup>11</sup> and is now available in various flavors in a wide variety of codes.<sup>12-15</sup> Implicit solvation models are very convenient and valuable when the main effect of the solvent is expected to be the stabilization of (partially) charged species such as in electrocatalysis as reviewed by Ringe et al.,<sup>16</sup> including when modelling transition states.<sup>17</sup> In the PCM, the average interaction between a solute and the solvent is modelled by two terms: an average electrostatic interaction that leads to a stabilization of the solute, supplemented by the so-called cavitation energy, which accounts for all the energy penalty terms (repulsion, creation of a cavity in the solvent etc.) While the electrostatic interaction can be computed by the Poisson-Boltzmann equation, the cavitation energy generally relies on semi-empirical parameters, fitted to molecular benchmark data.<sup>16</sup> In practice it turns out that the cavitation energy is generally negligible compared with the electrostatic interaction.<sup>18,19</sup> However, the definition of the solute cavity, and thus the transition of the dielectric constant from its vacuum value (in the solute) to the bulk solvent value, directly impacts the quality of the implicit solvent model,<sup>20,21</sup> including work functions<sup>22</sup> and adsorption energies.<sup>23</sup> While machine-learning seems to be able to replace implicit solvents for neutral molecules,<sup>24</sup> the lack of a physical description of electrostatics seems difficult to reconcile with electrified interfaces. The latter are, however, a stronghold of implicit solvents as recently reviewed in detail.<sup>25</sup> Indeed, the implicit solvent ensures a reasonable capacitance (relation between applied potential and surface charge)<sup>26</sup> and allows a consistent, black-box, treatment of the solvent for all reactants and intermediates,<sup>27,28</sup> equally applicable to water<sup>29</sup> and organic solvents.<sup>30</sup> As an example, we have exploited the implicit solvent model to investigate the electro-

chemical potential dependence of the electro-oxidation of formic acid, typical for direct formic acid fuel cells.<sup>29</sup> In this study we could demonstrate that the reaction mechanism on Ni(111) crucially depends on the reorientation of the formate intermediate, a formally “chemical” reaction step, which nevertheless shows a non-negligible potential dependence. This importance of the electrochemical potential on formally chemical steps has also been observed for the reductive coupling of CO<sub>2</sub> on copper,<sup>31</sup> suggesting the general importance of accounting for the electrode polarisation. We have also relied on an implicit solvent description to elucidate why increasing the pH increases thermal formic acid decomposition into CO<sub>2</sub> and H<sub>2</sub> on Pd(111).<sup>32</sup> At a pH above the pKa of formic acid, anionic formate can be chemisorbed at the Pd/water interface. Detailed analysis has revealed that the interaction between the surface dipole moment of the adsorbate with the electric field generated by the adsorption of anionic species results in a lowering of the limiting transition states. This study relied on the capability of rigorously computing the energy of a charged periodic surface through the inclusion of an effective neutralizing counter-charge, obtained by the solution of the linearized Poisson-Boltzmann equation.<sup>33</sup> Furthermore, we have demonstrated for two potential-dependent overlayers on Au(111) immersed in an aqueous electrolyte, that this approach yields semi-quantitative agreement with experiments,<sup>34,35</sup> a conclusion that has also been reached for CO<sub>2</sub> reduction intermediates over copper.<sup>36</sup> Therefore, we advocate the use of implicit solvents for investigating the potential dependence of electrocatalytic reactions,<sup>37</sup> including the reactivity on semi-conductors under photo-electrocatalytic conditions, such as oxygen evolution reaction (OER) over the CoOOH co-catalyst.<sup>38</sup> For this catalytic system we have demonstrated the importance of considering chemical steps, in particular the formation of the O–O bond and the desorption of O<sub>2</sub> and revealed the involvement of two, rather than only one, Co site for the most probable reaction pathway.

Water can also play a major role as a competitive adsorbate. To gain a thorough understanding of this effect, we need to *explicitly describe water molecules*. Moving to classical

molecular mechanics (MM) is then a natural choice to avoid the large computational burden associated with *ab initio* molecular dynamics. However, pair-wise force fields fail to properly describe chemisorption of intermediates relevant to Catalysis. Therefore, we have proposed a QM/MM approach (MMSolv) to keep a high-level (DFT) description of the surface/adsorbate interaction in combination with solvation effects at the MM level, similar in spirit to the work of the Heyden<sup>39</sup> and Getman<sup>40</sup> groups. In practice, MMSolv combines *ab initio* adsorption energies with solvation energies computed at the MM level using an alchemical transformation (see Fig. 1).<sup>18</sup> Of course, the reliability of the obtained results strongly depends on the quality of the force field. Most of the water/metal force fields do not reproduce the near chemisorption of the water/metal interaction observed with DFT.<sup>41</sup> Our GAL17 force field has been specifically designed to retrieve the strength and angular dependence of this interaction.<sup>41,42</sup> The water/metal interaction is strong enough to challenge the standard alchemical transformation, so that we had to pass through a well-behaved physisorption potential for Pt/water in order to achieve converged, reproducible results.<sup>43</sup> This MMSolv strategy has been validated against experimental data on the adsorption of aromatics at the Pt/water interface.<sup>43-45</sup> MMSolv performs noticeably better than PCM thanks to a proper inclusion of the surface solvation. It can be easily used with oxides surfaces, given that the chemisorption of water is well described.<sup>46</sup> When considering the adsorption of flexible molecules (e.g. polyols), MMSolv can easily be combined with our package DockOnSurf<sup>47</sup> to automate the sampling of conformers. Currently, MMSolv is, however, not directly applicable to the adsorption of ions, since an electrostatic embedding is missing.<sup>48,49</sup> Another limitation remains the quality of the classical force field. Our GAL force field<sup>41</sup> was a clear improvement compared to existing Pt/water force fields. Nevertheless, we have shown recently that many-body interactions (polarisability and the charge transfer) contribute up to about 50 % to the adsorption energy of water layers on Pt(111),<sup>50</sup> an effect that is beyond the capabilities of pair-wise additive GAL force fields. Importantly, the charge

transfer scales with the polarisability. Hence, developing polarisable force fields (e.g., in the spirit of AMOEBA<sup>51</sup>) could be a valuable approach to improve the description of metal/water interfaces.

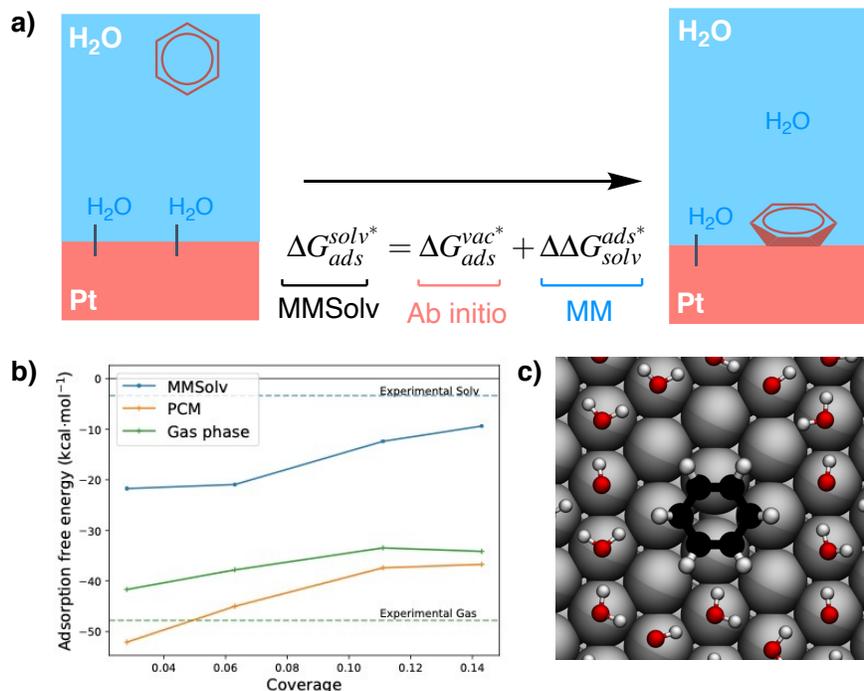


Figure 1: (a) Principle of the MMSolv method to compute adsorption energies at the water/solid interface (b) Gibbs free energy of adsorption of benzene at the Pt/water interface, simulation data from<sup>43</sup> and experimental data<sup>45</sup> (c) Snapshot of the Pt/water interface showing the first layer of hydration, extracted from MM simulations used in MMSolv.

An alternative to improve the description of the direct interactions between chemisorbed species and water is to add a few water molecules to be described at the *ab initio* level. This approach, often coined *micro-solvation*, has been originally used to describe solvation effects in homogeneous aqueous phase. For instance, micro-solvation was successfully used in combination with a PCM to compute the aqueous acid dissociation constants.<sup>52</sup> This is how we have investigated the impact of water on the transformation of oxygenated compounds catalysed by metals for the past 10 years.<sup>53–58</sup> Importantly, adding explicitly one water molecule has allowed us to rationalize solvent effects in ketone hydrogenation.<sup>56</sup> Figure 2 gathers the energetic profile of acetone hydrogenation on Ru(0001) and

on  $\text{H}_2\text{O-Ru(0001)}$  with the related structures. In presence of a H-bonded water molecule on  $\text{H}_2\text{O-Ru(0001)}$ , acetone and iso-propanol are more strongly chemisorbed thanks to the additional H-bonding with the chemisorbed water. In contrast, the iso-propoxy intermediate is triggered to move from the hollow site to a bridge site that resembles more closely the transition state configuration. For this reason, water accelerates the ketone hydrogenation on oxophilic metals, where alkoxy intermediates are found to be particularly stable and difficult to hydrogenate into alcohols (O–H bond formation) or dehydrogenate into ketones (C–H bond scission).<sup>53–56</sup> More recently, we have focused on the energetics of O–H, C–H, C–C and C–O bonds cleavages of alcohols on Pt(111). Despite the strong polarity of O–H and C–O bonds, modeling water as a polarisable continuum was not found to significantly impact on the activation and reaction energies compared with vacuum.<sup>19</sup> The largest modification is found for a C–C bond splitting ( $\text{CH}_3\text{–COH}$ ), with a decrease of 0.22 eV of the reaction energy. This can be related to a change in the orientation of the hydroxyl group that reduces its stabilizing interactions with PCM. To improve the description of H-bonding between the water solvent and the solute, we have systematically added one water molecule, preferentially chemisorbed on a neighbouring top site. In the presence of micro-solvation, the impact of water was considerably stronger than when using only PCM.<sup>58</sup> The largest effect we identified is an increase of 0.53 eV of the activation barrier of a C–O bond dissociation ( $\text{CH}_3\text{CH}_2\text{–O}$ ). This can be related to a stabilization of the initial state that is greater than the stabilization of the transition state. This example is representative of the dissociation of C–O bonds, but not of C–OH bonds. In this later case, the resulting OH fragment is stabilized through a very strong H-bond, which facilitates the C–OH bond cleavage. This micro-solvation approach can be used in a wide range of context to include the direct interactions between chemisorbed species and water, as for instance to address the competition between decarboxylation and decarbonylation in acetic acid over Pd(111),<sup>59</sup> to predict onset potentials in electrocatalysis,<sup>60</sup> or to study the adsorption of a corrosion inhibitor.<sup>61</sup>

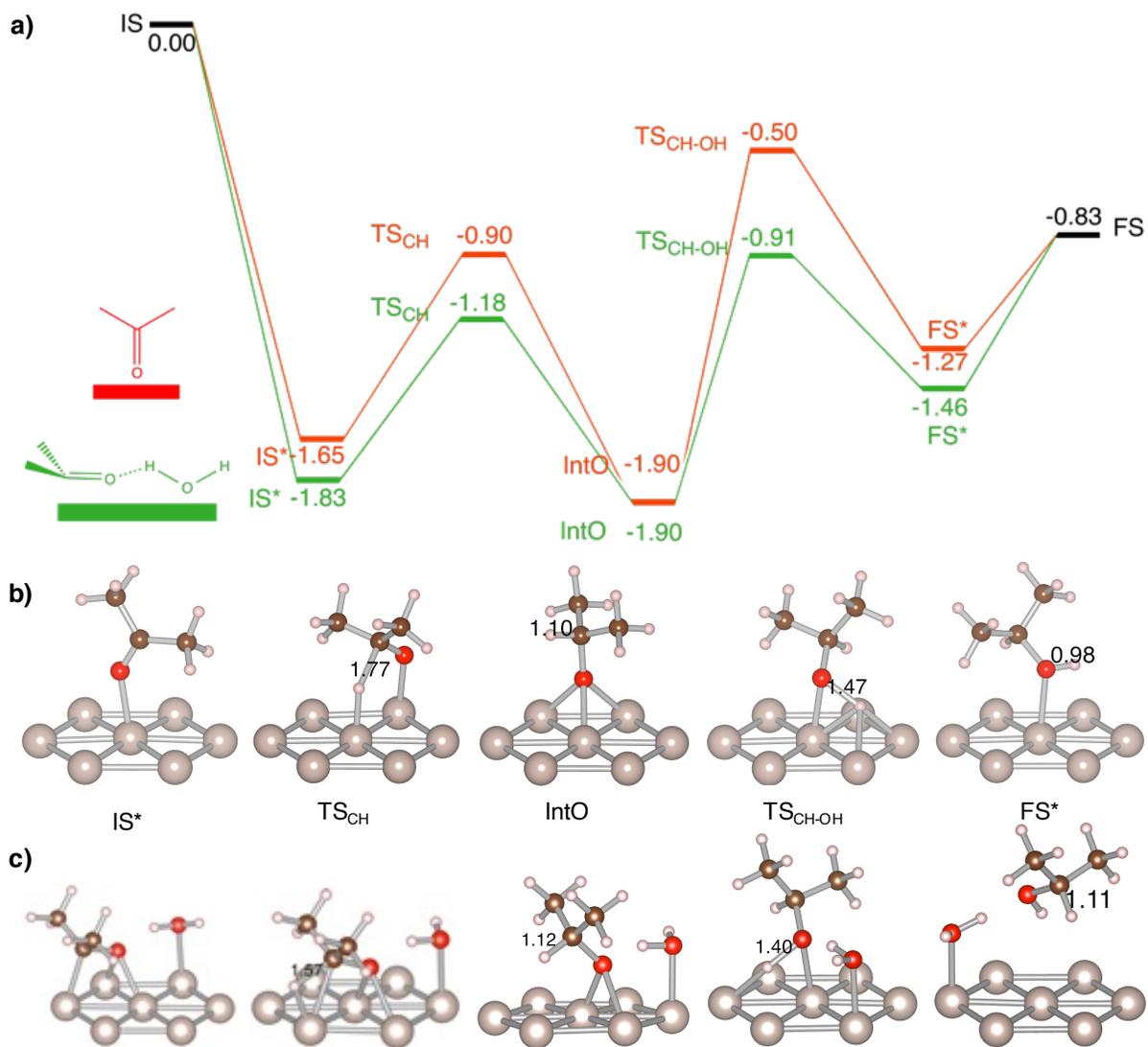


Figure 2: Acetone hydrogenation on Ru(0001) and H<sub>2</sub>O-Ru(0001) studied using the PW91 functional.<sup>56</sup> (a) Energy profiles in eV (b) Optimized structures on Ru(0001) (c) Optimized structures on H<sub>2</sub>O-Ru(0001). Main distances are indicated in Å.

For many reactions, *water is a non-innocent solvent*. In other words, its impact goes beyond the stabilization of surface species through electrostatic effects and H-bonding: water and other protic solvents can also react, act as a co-catalyst and modify the reaction mechanism.<sup>62</sup> This is well known in the catalytic oxidation of alcohols in water when using  $O_2$  as a oxidant. Isotopic labelling experiments have demonstrated that the oxygen atom that is incorporated in the carboxylic acid product is mainly coming from water and not from  $O_2$ .<sup>63</sup> The presence of water facilitates the  $O=O$  splitting not only thanks to a stabilizing H-bond network but also through a proton transfer. On Au(111), we have shown that a first proton is transferred from  $H_2O$  to  $O_2$  yielding OH and HOO. Then, the  $O-O$  bond cleavage in OOH is facilitated by a concomitant proton transfer from a second water molecule, generating in total 4 OH. These chemisorbed OH are the oxidizing species at the Au/water interface.<sup>57</sup> The presence of water facilitates the  $O_2$  activation on Au(111) since the overall barrier to generate the four OH is 0.86 eV while the  $O_2$  splitting into two chemisorbed O was found above 1 eV by Zope et al.<sup>63</sup> This barrier is even lower in presence of a base (0.74 eV), when the adsorption of a hydroxide anion polarises the Au/water interface.<sup>57</sup> Modeling the aqueous environment using micro-solvation has well-known limitations: the number and position of the water molecules has to be chosen, making its usage clumsy and the results can depend on these somewhat arbitrary choices in an unpredictable manner, in particular when proton-transfers are involved. Even combined with PCM, micro-solvation cannot properly describe solvation shells with changing size, the surface solvation or long-range proton transfers in water (Grotthus mechanism). Thus, moving to a *full ab initio description of the liquid water* is appealing, since in this case each water molecule could react. In principle, *ab initio* molecular dynamics (AIMD) addresses all the limitations we listed so far. However, the main bottleneck of AIMD is to reach a representative phase-space sampling, which requires sufficiently long MDs. Recently, the usefulness of AIMD for heterogeneous catalysis at the water/solid interface has significantly increased thanks to enhanced-sampling methods and efficient compu-

tational resources and softwares. For instance, AIMD can be enhanced using thermodynamics integration or umbrella sampling, which require a good pre-knowledge of the reaction coordinate.<sup>62</sup> This is how Siemer et al.<sup>64</sup> demonstrated that the O<sub>2</sub> bond cleavage barrier catalysed by Au<sub>11</sub> nanoparticle supported over TiO<sub>2</sub> is decreased by 25% in aqueous phase relative to the gas phase. In this study, a full slab of liquid water (80 water molecules) is added on top the Au<sub>11</sub>/TiO<sub>2</sub> system, and the O–O distance is a natural choice for the reaction coordinate. However, thermodynamic integration is limited to a single reaction step,<sup>65</sup> and the reaction coordinate needs to be straightforward. For instance, in the O<sub>2</sub> dissociation case, the H transfer is only observed if it happens in the reachable timeframe (< 20 picoseconds). We recently faced this issue when attempting to describe the desorption of ethanol from the alumina/water interface to the bulk water.<sup>66</sup> It turned out to be a challenging process for thermodynamic integration because of the very slow dynamics of interfacial water molecules.<sup>67</sup> We employed the altitude as the natural reaction coordinate. The gas-phase adsorption mode and site was taken as a starting configuration for a slow-growth AIMD. Still, the replacement of chemisorbed ethanol by chemisorbed water (or dissociated water) requires a strong reorganisation of the solvation shell that cannot be reached in the accessible time frame, yielding to a spurious barrier. A first solution is to trigger this reorganisation “by hand”, making the assumption that water diffusion at the interface is much faster than the desorption. However, the water diffusion is considerably slowed down at the interface compared to the bulk solution,<sup>67</sup> so that the validity of this hypothesis is uncertain. An alternative is to move to metadynamics,<sup>68</sup> where additional reaction coordinates can be included to bias (and thus accelerate the sampling of) changes in solvation.<sup>66</sup>

Last, water can even modify the catalyst surface. For instance, combining explicit water molecules and an implicit solvent model, we have provided evidence that sulfur atoms on edges of MoS<sub>2</sub> will be gradually replaced by hydroxyl groups under hydrogen evolution reaction conditions.<sup>69,70</sup> Complementing the micro-solvation with a continuum

model has been mandatory in this case to properly describe the polarisation of the electrified interface. This combination of micro-solvation and PCM is a valuable tool to investigate the stability of active sites in aqueous solution but it cannot easily determine the corresponding activation energies and thus might miss kinetic bottlenecks. Furthermore, how a robust combination of implicit and explicit solvation can be achieved at electrified interfaces remains a subject of active research,<sup>71</sup> last but not least because the implicit solvent should not penetrate between the explicit solvent molecules.<sup>72</sup> Accelerating the phase-space exploration along several variables, *ab initio* metadynamics enables modelling of such multi-step complex reactions at the catalyst/water interface as demonstrated on the first steps of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> hydrolysis.<sup>73</sup> The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(110) surface exposes two tetrahedral aluminum atoms (Al <sub>$\alpha$</sub>  and Al <sub>$\beta$</sub> ) in contact with water.<sup>74</sup> During hydrolysis, the coordination number (CN) of these aluminum atoms with water should increase, while the CN with the oxygen of alumina should decrease. Using these two variables, we explored the reactivity of the two tetrahedral aluminum atoms and identified the most sensitive Al atom on the (110) surface (named Al <sub>$\beta$</sub>  in Figure 3). The two-dimensional free energy surface landscapes are shown in Figure 3. While only one free energy well is obtained when biasing the CNs of Al <sub>$\alpha$</sub> , several wells are obtained when biasing the CNs of Al <sub>$\beta$</sub> , demonstrating that Al <sub>$\beta$</sub>  is the weak-spot for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> decomposition via hydration. The corresponding free energy surface provides the mechanism (addition/elimination sequence) and the barriers ( $\sim 80$  kJ·mol<sup>-1</sup>, see Figure 3d).

*Ab initio* metadynamics appears as the method of choice when water is involved as a reactant. Still, it is challenging to set up since the description of the reactions relies on only few variables to describe complex multi-step mechanisms. For cases where water is not reacting, we have recently developed MMSolv, a hybrid scheme that combines *ab initio* adsorption energies with solvation energies at the MM level. Compared with PCM, MMSolv accounts for the competitive adsorption of the water solvent without the arbitrariness of micro-solvation. Just like enhanced AIMD, MMSolv computes the properties

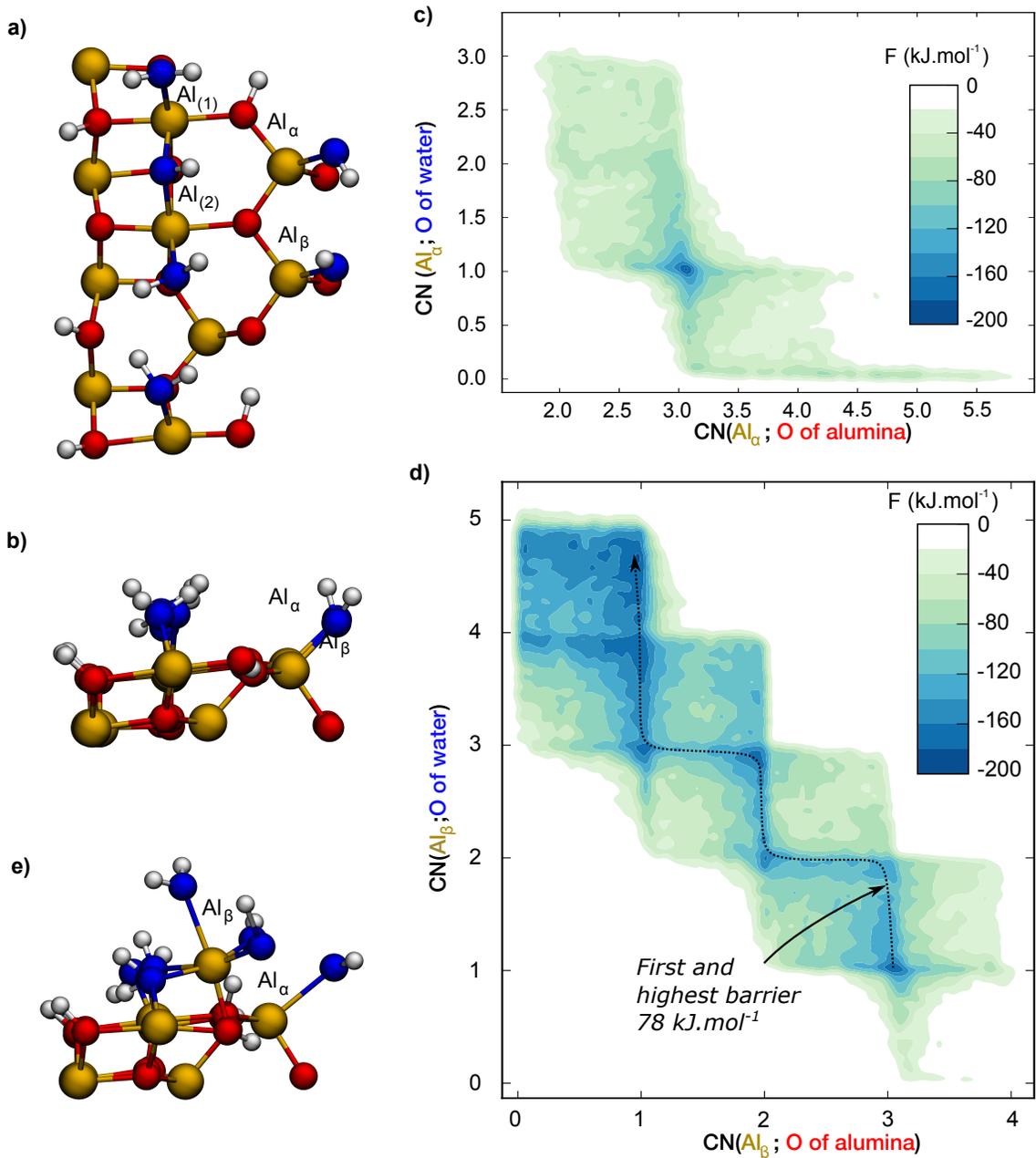


Figure 3: Exploration of the reactivity of  $\gamma$ - $\text{Al}_2\text{O}_3(110)$  in contact with a slab of liquid water.<sup>73</sup> Top view (a) and side view (b) of the initial structure. Only chemisorbed water molecules are shown.  $O_{\text{wat}}$ ,  $O_{\text{alumina}}$ , Al, H in blue, red, yellow, white respectively. Bi-dimensional free energy surfaces obtained from *ab initio* metadynamics when exploring the reactivity of the tetrahedral aluminum  $\text{Al}_\alpha$  (c) and  $\text{Al}_\beta$  (d). Side view of the final structure (e) with a hydrated  $\text{Al}_\beta$  extracted from the alumina network.

for liquid water at room temperature, but is computationally much cheaper and gives easily access to the solvation energies of arbitrary adsorbates. MMSolv relies on MM and alchemical transformation to compute the solvation term. So far, it implements a basic mechanical embedding but it could be upgraded to an electrostatic embedding, in particular to be used for electrified interfaces and the adsorption of ions. A more serious drawback is that the reliability of the results strongly depends on the quality of the force field. Therefore, more accurate force fields are clearly needed. Regarding water/metal force fields, a first step is to move to polarizable force fields. This was recently proposed by Goddard and co-workers in the context of electrocatalysis.<sup>75</sup> Another possibility is to move to machine learning potentials<sup>76</sup> as proposed by Behler and co-workers to describe the Cu/water interface,<sup>77</sup> a strategy that has lead to valuable insight into the hydrogen coupling at the platinum/water interface.<sup>78</sup> Still, these accurate potentials lack transferability and cannot be used directly to investigate how an adsorbate would be solvated or could react at this aqueous interface. Nevertheless, a system-specific machine-learning potential in combination with DFT resampling<sup>79</sup> allows to retrieve most of the solvent effects, albeit at a considerable computational cost. Furthermore, such schemes result in complex workflows, which require automatization in order to become viable for applications.<sup>80</sup> Reactive force fields are a good alternative to handle complex interfaces. Once parameterized, they are fast enough to simulate 1 ns. For instance, ReaxFF has recently been used to investigate the dissociative adsorption and decomposition of acetic acid at the ZnO/water interface in function of the temperature.<sup>81</sup> Moreover, such simulations also give access to the entropy at the solid/water interface,<sup>82</sup> which will ultimately enable a fundamental understanding of the thermodynamic differences in reactivity between gas-phase, solution-phase and the water/solid interface.

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## Graphical TOC Entry

